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ROLES OF CRYSTAL FIELDS IN MAGNETIC SUPERCONDUCTING RARE-EARTH RHODIUM BORIDES

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INTRODUCTION

Many interesting magnetic as well as superconducting properties have been reported in a series of rare earth (R) rhodium borides RRh_4B_4. Nonmagnetic $LuRh_4B_4$ and YRh_4B_4 are high T_c superconductors with $T_c \sim 11.5$ K and ~ 11.3 K, respectively.[1] On the other hand, RRh_4B_4 with R = Gd, Dy, Tb, and Ho are ferromagnetic metals.[1] Furthermore, $ErRh_4B_4$[2,3] and the pseudoternaries such as $Er_{1-x}Gd_xRh_4B_4$,[4] $Er_{1-x}Ho_xRh_4B_4$,[5] $Ho_{1-x}Lu_xRh_4B_4$,[6] $Gd_{1-x}Y_xRh_4B_4$,[4,7] $Er_{1-x}Tm_xRh_4B_4$,[8] and $Er_{1-x}Y_xRh_4B_4$[9] are reentrant superconductors in proper ranges of x; the superconducting states change to ferromagnetic normal states at low temperatures.

The crystal structure[10,11] has tetragonal symmetry, with the ratio of unit cell axial length c/a being around 1.4. The rare earth ions form a body centered tetragonal lattice in RRh_4B_4. Superconductivity is strongly related to the lattice structure.[11] Recently, it has been demonstrated[12] by using α-particle irradiation techniques that the ferromagnetic as well as superconducting transitions in $ErRh_4B_4$ are strongly dependent on the extent of damage in samples.

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Among the structural effects on superconductivity and magnetism in RRh_4B_4, we discuss in this paper those of the tetragonal crystal field of rare earth ions on both magnetic and superconducting properties. Special attention is paid to RRh_4B_4, with R = Ho, Er, and Tm, and the pseudoternaries $Er_{1-x}Ho_xRh_4B_4$ and $Er_{1-x}Tm_xRh_4B_4$. The lattice constants in the systems are practically independent of the ions[10,13] so that we may concentrate on the crystal field effects and neglect the other structural effects on superconductivity and magnetism. We consider only the lowest crystalline anisotropy field in order to render our discussion transparent. Irrespective of the simplicity of the model, we find semi-quantitative agreement with experiments of (i) the reduced value of the ground state moment in $ErRh_4B_4$, (ii) the phase diagrams of $Er_{1-x}Ho_xRh_4B_4$ and $Er_{1-x}Tm_xRh_4B_4$, and (iii) the critical concentration x_{cr} at which the reentrant transition disappears in $Ho_{1-x}Lu_xRh_4B_4$, $Er_{1-x}Tm_xRh_4B_4$, and $Er_{1-x}Y_xRh_4B_4$.

THEORETICAL BACKGROUND

The original idea for studying, on an equal basis, the effects of both crystal field and magnetic ordering on superconductivity may be found in the argument by de Gennes and Sarma.[14] We take the crystal field interaction

$$H_{cf} = -2I \int d^3\vec{r} \left[g(r) - 1\right] \vec{J}(\vec{r}) \cdot \vec{s}(\vec{r}) \quad , \tag{1}$$

where I is the exchange constant, $\vec{J}(\vec{r})$ is the total angular momentum of a rare earth ion at position $\vec{r}$ with Landé g-factor $g(r)$, and $\vec{s}(\vec{r})$ is the spin operator of a superconducting electron at $\vec{r}$. Let us define the fictitious field at space-time $\vec{r}'$ and t',

$$\vec{h}(\vec{r},t) = 2I\left[g(\vec{r}) - 1\right]\vec{s}(\vec{r},t) \quad . \tag{2}$$

It induces the polarization of the rare earth ion at $\vec{r}'$ and t',

$$\vec{J}(\vec{r},t) = \chi(\vec{r}-\vec{r}', t-t')\vec{h}(\vec{r},t) \quad , \tag{3}$$

where $\chi(\vec{r}, t)$ is the susceptibility tensor (more strictly speaking, the time-dependent correlation function) of the rare earth ions. Inserting Eqs. (2) and (3) into Eq. (1), we find the effective interaction between conduction electrons as

$$-\vec{h}(\vec{r}',t)\chi(\vec{r}-\vec{r}', t-t')\vec{h}(\vec{r},t)$$

$$= -4I^2\left[g(\vec{r}) - 1\right]\left[g(\vec{r}') - 1\right]\vec{s}(\vec{r}',t)\chi(\vec{r}-\vec{r}', t-t')\vec{s}(\vec{r},t) \tag{4}$$

In the disordered (paramagnetic) states of the rare earth moments, the susceptibility $\chi(\vec{r}-\vec{r}', t-t')$ and its Fourier transform $\chi(\vec{r}-\vec{r}',\omega)$ are positive so that the interaction (Eq. (4)) is repulsive for antiparallel spins of two electrons. Therefore, superconductivity is suppressed by localized magnetic moments. Although the mathematical treatment is quite similar to that of the electron-phonon interaction, the non-local character of the interaction (Eq. (4)) is not neglected.[15,16] The exchange interaction between localized moments affects superconductivity through the non-local characters of both the susceptibility and a Cooper pair.

Also important is the energy dependence of the interaction. Not only the exchange interaction but the crystal field determine the dynamics of the susceptibility. Because the superconducting electrons are in the range of twice the phonon Debye energy $2\omega_D$ measured from the Fermi energy (the most involved range is $\sim 4T_c$), the susceptibility in Eq. (4) which contributes to the superconductivity is restricted within the range of energy. Let us consider a magnetic impurity with a singlet ground state separated from the excited states by the energy ω_0. If ω_0 is much larger than $4T_c$, the interaction between the impurity and the superconducting electrons has no effect on the superconducting transition, because the susceptibility at low energy in Eq. (4) is small. On the other hand, if ω_0 is of the order of or less than $4T_c$, the interaction suppresses T_c as a static magnetic potential does.[17] The complete theoretical study of the effect of a magnetic impurity with crystal-field-split energy levels on superconductivity has been done by Fulde et al.[18,19] by using the quasi-fermion formalism introduced by Abrikosov.[20] It is also useful to describe the effects of magnetic ions by using the dynamical susceptibility: the exchange interaction between magnetic ions as well as the crystal field are systematically taken into account on an equal basis.[15,8] In the quasi-fermion formalism, it is very difficult to introduce the interaction between magnetic ions.[20]

CRYSTALLINE ANISOTROPY IN RARE EARTH RHODIUM BORIDES

In this and the following sections, we are concerned with RRh_4B_4. The tetragonal structure introduces the uni-axial crystal field,

$$\mathcal{H} = DJ_z^2 \,, \tag{5}$$

where the tetragonal axis is taken to be the z-axis. Here, D is the crystal field parameter of the rare earth ion with angular momentum $\vec{J}$. The point charge model[21] gives the relation $D = \alpha A\langle r^2\rangle$, where α is the Stevens factor, A is a parameter that depends on the crystal structure and is expected to be positive, and $\langle r^2 \rangle$ is the average value of the 4f wave functions of the rare earth ion. One indication of the crystal-field energy splitting is seen in the experiments on the specific heat:[22,23] the magnetic part of the specific heat in $Er_{1-x}Gd_xRh_4B_4$ (x = 0, 0.09, and 0.28) has a Schottky peak around 10 K. Since Gd^{3+} ions are in the S-state, we calculate the value of D of Er^{3+} ions in RRh_4B_4 to be +5 K. Here, we note that the sign of D is due to α. $ErRh_4B_4$ is ferromagnetic below $\sim$ 0.9 K. The magnetic moment is in the c-plane,[3] a fact which supports the crystal field model.

The static moment in $ErRh_4B_4$ extrapolated to 0 K has been measured to be 5.6 μ_B per Er^{3+} ion by a neutron experiment.[3] This value is much smaller than the free-ion value of 9 μ_B and the value of 9.6 μ_B, which has been estimated from the magnetic susceptibility measurements.[2] We ascribe this reduction of the static moment to the crystal field: the ground electronic states in Er^{3+} ions have the values $J_z = \pm 1/2$. The lowest excited states with $J_z = \pm 3/2$ are separated from the ground states by the energy 2D $\sim$ 10 K, which is much larger than the exchange energy of the order of the ferromagnetic transition temperature T_M. Therefore, the magnetic properties at low temperatures are mainly determined by the ground electronic states. We take the direction of the magnetic moment in the c-plane below T_M to be the x direction. Because the x component of the angular momentum J_x in the space of $J_z = \pm 1/2$ is given by

$$J_x = \begin{pmatrix} 0 & 4 \\ 4 & 0 \end{pmatrix} ,$$

and because g = 6/5, the contribution of the ground states to the magnetic moment at 0 K is calculated to be $g\langle J_x \rangle \mu_B$ = 4.8μ_B. This value reproduces 86% of the observed value and is satisfactory.

In contrast to Er^{3+} ions, Ho^{3+} ions have negative D, with the value of −5 K because α is negative. Thus, the direction of the magnetic moment in ferromagnetic $HoRh_4B_4$ is in the tetragonal direction.[24] The electronic ground states of Ho^{3+} ions have the values of $J_z = \pm 8$ and the energy of the excited states measured from the ground states is much larger than $T_M \sim$6.6 K. Therefore, Ho^{3+} ions may be taken as Ising spins with S = 1/2. Tb^{3+} and Dy^{3+} ions will also behave like Ising spins with S = 1/2 because it is expected that the sign of D in these ions is negative.

PSEUDOTERNARIES $Er_{1-x}Ho_xRh_4B_4$ AND $Er_{1-x}Tm_xRh_4B_4$

Johnston et al.[5] have observed the ferromagnetic transition temperature T_M in the pseudoternary system $Er_{1-x}Ho_xRh_4B_4$ along with T_C as functions of x. One of their interesting observations is that the T_M vs x curve has a minimum. We have calculated the curve in this system using mean field theory. The RKKY mechanism for the exchange interaction between magnetic ions is assumed. One exchange constant is determined from T_M in $HoRh_4B_4$. Then, the remaining exchange constants are obtained by scaling the de Gennes factors.[8,25] The calculated T_M vs x is given in Fig. 1 together with the theoretical T_C vs x curve. In the figure, the experimental results by Johnston et al.[3] are reproduced for comparison. We find that the minimum of T_M is identified as the tetracritical point. In the calculation it was assumed

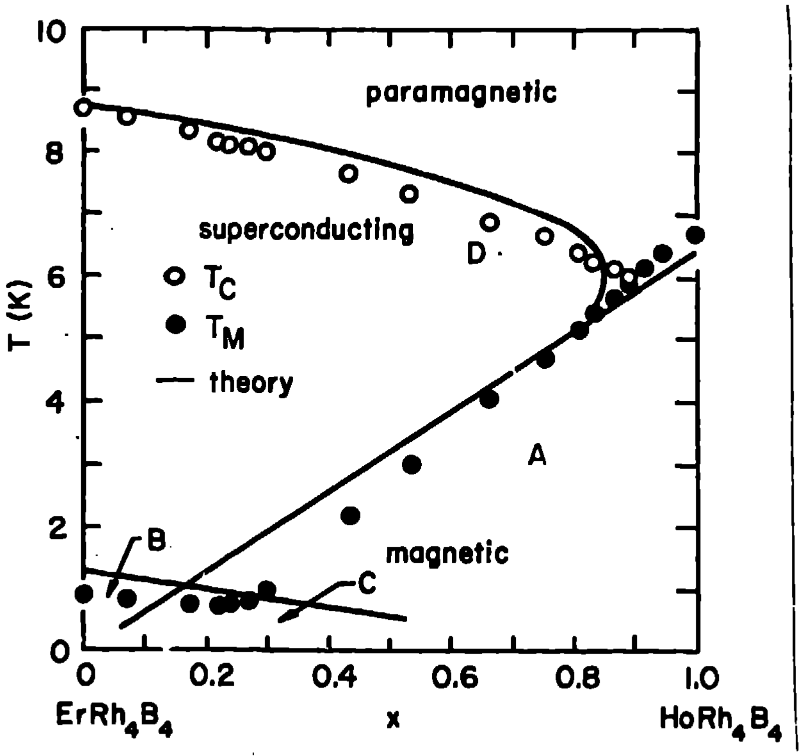

Fig. 1. Phase diagram for $Er_{1-x}Ho_xRh_4B_4$. Phase A: ferromagnetic with the magnetization in the tetragonal direction, Phase B: ferromagnetic with the magnetization perpendicular to the tetragonal direction, Phase C: oblique ferromagnetic (mixed ferromagnetic), and Phase D: paramagnetic or superconducting. The data points are taken from Johnston et al.[18]

that the tetracritical point is the decoupled one.[26] We note that the value of T_M in $ErRh_4B_4$ has been calculated quite well using the RKKY mechanism and the crystal field model, with results consistent with those of the structural study by Rowell et al.[12] More detailed discussion of T_c and T_M will be given in a separate paper.[8]

The value of the crystal field parameter D for Tm^{3+} ions is calculated to be +23 K. Tm^{3+} ions are non-Kramers ions (J = 6) so that the ground state is a singlet state with J_z = 0. Because the RKKY interactions between Tm^{3+} ions and between Tm^{3+} and Er^{3+} ions are much weaker than the energy of the first excited states ($J_z = \pm 1$),[8] Tm^{3+} ions remain in the nonmagnetic ground state in $Er_{1-x}Tm_xRh_4B_4$. The experimental results given in Fig. 2 are consistent with this conclusion; T_M decreases with increasing x and above $x_{cr} \sim 0.43$, no ferromagnetic state is observed down to 0.075 K. The theoretical T_M is the object of the next section.

The T_c vs x curve in $Er_{1-x}Tm_xRh_4B_4$ (Fig. 2) shows the different properties of Tm^{3+} ions; T_c depends linearly on x, and the values in $ErRh_4B_4$ and $TmRh_4B_4$ are respectively 8.7 K and 9.6 K, which are lower than T_c in

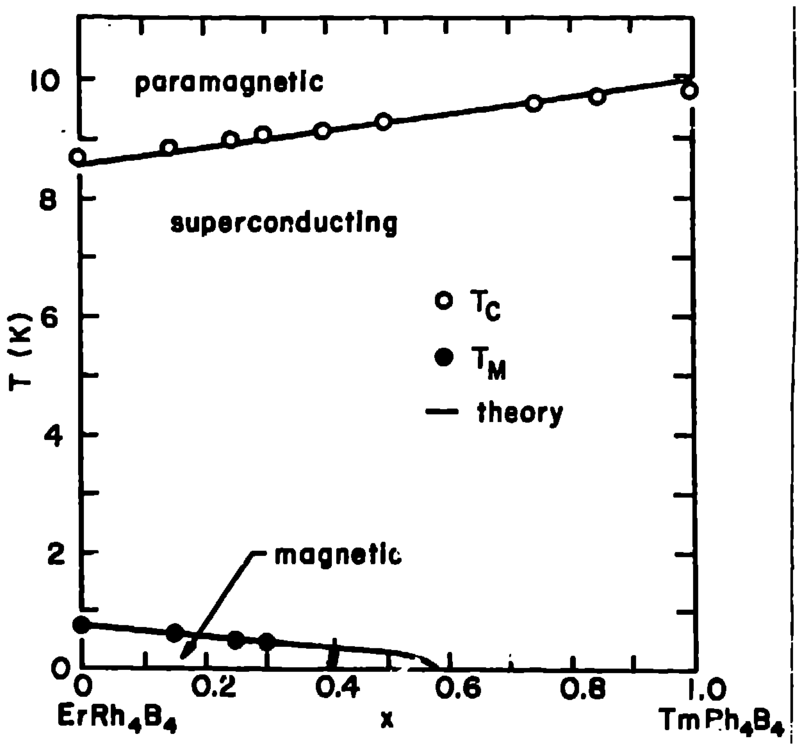

Fig. 2. Phase diagram for $Er_{1-x}Tm_xRh_4B_4$.

nonmagnetic $LuRh_4B_4$ and YRh_4B_4. Because the lattice constants in $Er_{1-x}Tm_xRh_4B_4$ are close to those in $LuRh_4B_4$,[10,13] we may conclude that Tm^{3+} ions act as pair breakers on T_c with the value $(g-1)J$ of 1, as Er^{3+} ions do with $(g-1)J = 3/2$. We remember the argument given in the second section: because $4T_c$ is larger than the crystal field value, Tm^{3+} ions act as magnetic ions on T_c. We have found that Tm^{3+} ions behave as magnetic on T_c and as nonmagnetic on T_M. This fact is instructive for the study of inelastic properties of the magnetic ions with crystal-field-split energy levels.

CRITICAL CONCENTRATION FOR REENTRANT TRANSITION

It has been observed[27] in $Er_xHo_{1-x}Rh_4B_4$ that the superconducting-to-ferromagnetic transition is slightly first order. We may understand this observation as follows: the superconducting state is the Meissner (Type I) state at the transition.[28] The long-ranged parts of the ferromagnetic exchange interaction between magnetic moments are suppressed in the Meissner state because of the existence of the energy gap (not necessarily finite) so that the magnetic energy is different from that in the normal state.[29-31,16]

We take the nearest-neighbor exchange interaction in the Meissner state and approximate the body-centered tetragonal lattice by a bcc lattice. Further approximating Er^{3+} moments to be Heisenberg spins, we have calculated the T_M vs x curve in $Er_{1-x}Tm_xRh_4B_4$ using the effective Hamiltonian method of statistical mechanics.[15,32,33] The results are given in Fig. 2. We find $\sim$ 0.57 to be the critical concentration x_{cr} of nonmagnetic ions above which there exists no reentrant transition. This value is compared with the experimental one of $\sim$ 0.43. However,[9] x_{cr} in $Er_{1-x}Y_xRh_4B_4$ has been observed by Okuda et al.[9] to be 0.57, which is in agreement with the theoretical value. Maple et al.[6] have observed x_{cr} in $Ho_{1-x}Lu_xRh_4B_4$ to be 0.72, larger than in the Er compounds mentioned above. We remember that Ho^{3+} ions behave like Ising spins in RRh_4B_4. For Ising spins in a bcc lattice x_{cr} is calculated to be 0.79.[33] This theoretical value is close to the experimental one by Maple et al.[6] We have found that x_{cr} for the reentrant transition is one indication of the fact that the ferromagnetic exchange interaction is short ranged in the Meissner state. The x_{cr} also depends on the crystal field because of the statistical effect. We note that the absence of the reentrant transition above x_{cr} does not neglect other magnetic states than the ferromagnetic state. It has been found[7] that the magnetic ground state above x_{cr} in the superconducting $Gd_{1-x}Y_xRh_4B_4$ is a spin-glass state. It would be interesting to study the magnetic ground states above x_{cr} in the superconducting $Ho_{1-x}Lu_xRh_4B_4$ and $Er_{1-x}Y_xRh_4B_4$.

DISCUSSION

In this paper, we have discussed the effects of the crystal field of rare earth ions due to the tetragonal crystal structure in RRh_4B_4 on the magnetic and superconducting properties. The uni-axial crystal field introduced in Eq. (5) is the simplest one so that a quantitative study is not justified. Nevertheless, we have found that the existing experimental data are understood quite well on the basis of the model. Also we conclude that the reentrant transition and the coexistence of superconductivity and magnetism depend on the crystal anisotropy field.

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